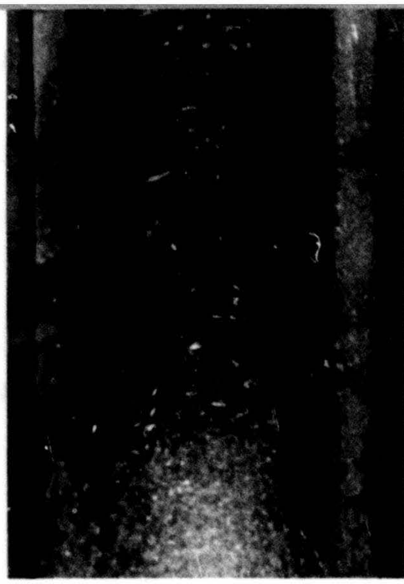

Technical Report

R 766

NAVAL CIVIL ENGINEERING LABORATORY

Port Hueneme, California 93043

Sponsored by

NAVAL FACILITIES ENGINEERING COMMAND

April 1972

FIELD IDENTIFICATION OF WEATHERED PAINTS

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FIELD IDENTIFICATION OF WEATHERED PAINTS

Technical Report R-766

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by

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ABSTRACT

A simple procedure and test kit have been developed for identifying the generic type and general composition of cured or weathered paint films. The procedure includes pyrolytic and burning tests, solubility tests, and tests for the detection of such elements as chlorine, nitrogen, lead, and mercury. All the tests can be performed with simple equipment by field personnel having little or no prior laboratory experience. The procedure and test kit were proven by successfully identifying 61 weathered paints that might be encountered at Naval shore activities.

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INTRODUCTION

The Naval shore activity has encountered deterioration problems where identifying the generic type or general composition of weathered paints would be helpful. For example, an activity needs to determine the compatibility of a weathered paint with a proposed topcoat, or an activity needs to determine the cause of a premature paint failure or to verify that the specified paint was used. Therefore, the Naval Facilities Engineering Command (NAVFAC) requested that the Naval Civil Engineering Laboratory (NCEL) develop a portable test kit and identification procedure that could be used in the field to identify weathered paints.

The perfect system for paint identification would lead to the specification number or proprietary name of a weathered paint. Unfortunately, it is impossible to devise such a system because of the thousands of paints used and the requirement that the kit and procedure be simple and suitable for field use. There are approximately 500 active military and Federal specifications for paints, many of which permit considerable latitude in the chemical compositions. Even an authentic manufacturer's list of all of the ingredients of a paint would not necessarily enable one to distinguish it from paints of the same general composition. It seemed prudent, therefore, to restrict the effort to the development of a kit and procedure that would identify the general type and general composition of cured or weathered paint films. Also, it was decided to investigate only those paints commonly used by shore activities and only those tests that might be conveniently and rapidly performed with simple equipment by persons having no formal training in chemistry. It was intended that the tests be designed for field use rather than for legal purposes. Should such detailed documentation be needed, suitable identification could be made only with more sophisticated equipment, such as described by Drisko and Crilly in Reference 1.

CLASSIFICATION OF WEATHERED PAINTS

One difficulty encountered in identifying a weathered paint* is the lack of a systematic recording of paints applied at the Naval shore activity. Also, military and Federal specifications for paints are listed in a rather

* In this report the word paint will be used to include protective coatings

random order;[2] in a technical manual,[3] the specifications may be grouped together according to their intended use, such as paints for the exterior surfaces of wooden buildings. Such an arrangement is useful, but it may be of limited value in identifying paints on the basis of their composition.

Most of the commonly used paints are of organic composition. These paints can be divided into four classes according to the processes involved in their curing: namely, (I) oxygen curing, (II) solvent drying, (III) water drying, and (IV) chemically reacting multicomponent paints. There are also some widely used, specialized, inorganic materials that can be grouped together as a single class (V). Therefore, paints can generally be divided conveniently into five broad classes.

Each of the five broad classes of paints can be further divided into subgroups or generic types on the basis of their nonvolatile vehicle (binder or resin). For example, paints containing vinyl resins are frequently called vinyls; those containing alkyd resins, alkyds; etc. The volatile vehicle (solvent or dispersant) is lost by evaporation and cannot be used for classifying or identifying cured or weathered paint films; but pigments, such as those containing lead, might on occasion be employed for that purpose.

Table 1 classifies paints into the five basic classes, and further subdivides them into numerous "generic types" based on the composition of the nonvolatile vehicles they contain. The classification is not perfect, because the curing of some paints involves more than one process, and some paints contain more than one type of resin.[4] For example, vinyl lacquers usually contain some polyvinyl acetate in addition to polyvinyl chloride. Nevertheless, the paints used at shore activities can nearly always be assigned to one of the basic classes of Table 1 and usually to one of the subclasses or generic resin types.

COLLECTION OF TEST SAMPLES

Sixty-one samples of weathered or cured paints that might be encountered at shore activities were collected to evaluate the paint identification tests. More than half of them were obtained from buildings or test panels exposed at Port Hueneme for 10 to 16 years as part of previous NCEL investigations.[5,6] The other samples were prepared by applying the paints to small glass or aluminum dishes. They were cured for at least 3 weeks before the chemical tests were performed and for at least 6 months before the solubility tests were performed.

Table 1. Classification of Paints Frequently Used at Shore Activities

Basic Class	Generic Type
I Air-oxidizing drying oils	Unmodified oil Alkyd Phenolic or other modified oil
II Solvent drying lacquers	Polyvinyl chloride Vinylidene chloride–acrylonitrile (saran) Polyvinyl butyral Chlorinated rubber Coal tar Asphalt Nitrocellulose Vinyl toluene–butadiene
III Water drying latex paints	Polyvinyl acetate Acrylic
IV Chemically reacting, multicomponent paints	Epoxy Coal tar epoxy Urethane Polyester
V Inorganic (noncombustible) paints	Silicates Flame-sprayed metals

Initially, a grinding tool was employed to remove the weathered paints, but it dug too deeply into the film. The procedure finally adopted was to scrape with a knife blade or sand a thin layer from the surface and to brush the paint fragments into a plastic container modified for this purpose (Figure 1). Notches approximately 1 x 1/8 inch were cut in the lips of the lower halves of the containers. The sandings and scrapings were then easily brushed into the containers through the openings formed by the notches. When the covers were placed on the containers, the notched openings were no longer exposed, and the weathered paint samples were stored securely. A clean envelope can also be used for collecting a specimen.

TEST METHODS

Many simple tests were investigated for the identification of paints. Some were previously reported spot tests[7,8] for chemical groups that could be used directly; others were modified from the original method; and still others were original methods devised at NCEL. Each pertinent test procedure is discussed below, with the actual test procedure and results given in Table 2.

Figure 1. Collecting samples of weathered paint.

Pyrolysis Test (T-1)

When fragments of weathered organic paints are heated rapidly in a container with limited access to air (Figure 2), destructive distillation occurs.[7] The resulting changes can involve melting, dehydration, hydrolysis, pyrolytic cleavage, oxidation, or a combination of these. Inorganic materials, on the other hand, show little or no change upon rapid heating.

The changes that occur to organic resins during pyrolysis can be used to reveal their identify. The amount of smoke and tar produced is related to the chemical structure of the resin (for example, aromaticity, molecular weight, and extent of cross linking). Nitrocellulose resins rapidly decompose upon heating.

A very specific and useful pyrolysis phenomenon occurs with alkyd resins that contain polyesters of ortho-phthalic acid (very common). Phthalic anhydride forms during heating in a test tube and distills and condenses as needle-shaped crystals on the upper, cooler portion of the tube (Figure 3). Crystal formation can be slow, but it can be accelerated by cooling the tube and scratching the inner wall with a glass rod.

Table 2. Test Procedures for Identifying Weathered Paint Samples

Identification	Test Procedure	Visual Observation		Conclusion
		Code	Description	
Pyrolysis test (T-1)	Place a small amount of weathered paint in a small pyrex test tube. Slowly bring bottom of tube into flame and heat it cautiously. Bottom of tube may become momentarily red hot, but the upper portion should be cool enough to condense vaporized liquids or solids. If burning occurs, extinguish it by covering the mouth of the tube. Observe changes; when changes subside, remove test tube from flame. When tube has cooled, scratch upper interior surface of tube with a glass rod to promote crystal growth. Check for casein or polysulfide resin by placing a moist strip of lead acetate paper in the fumes expelled during pyrolysis.	R-1.1	No trace of tar or smoke	Paint is in Class V
		R-1.2	Paint resin decomposed rapidly	Resin is nitrocellulose
		R-1.3	Needle-shaped crystals on upper portion of tube	Resin is an alkyd containing ortho-phthalate esters, or is a very much less common ortho-phthalate polyester
		R-1.4	An abundance of tar	Paint is not in Class III or V
		R-1.5	Relatively small quantity of tar	Paint is probably in Class II or III
		R-1.6	Moist lead acetate paper rapidly darkened in fumes	Paint contains casein, polysulfide, or other sulfur-containing compound
Solubility test (T-2)	Place a few chips or grindings of weathered paint into two different wells of a glass or porcelain spot plate. Add a few drops of benzene to one well and a few drops of methylethyl ketone to the other. Attempt to dissolve the paint sample by mixing with a thick glass rod. Use a hand magnifying lens to determine solubility by the dispersion of the pigment. Swelling of the binder should not be confused with dissolving.	R-2.1	Binder is soluble in methylethyl ketone	Paint is in Class II
		R-2.2	Binder is soluble in benzene	Paint is in Class II
		R-2.3	Binder is insoluble in either solvent	Paint is not in Class II
		R-2.4	Solvent is changed to a dark brown	Suggests the presence of coal tar or asphalt
		R-2.5	Binder is not readily soluble in dry methylethyl ketone, but immediately dissolves when a little water is added	Resin is polyvinyl butyral
Beilstein test for chlorine (T-3)	Heat a small porcelain boat (held by pliers) in a nonluminous flame until flame is no longer colored. Cool the boat, add a small sample of weathered paint, and cover it with copper oxide wire fragments. Place boat in edge of flame and observe any color change in the flame.	R-3.1	Green color imparted to flame	Presence of chlorine
		R-3.2	Green color not imparted to flame	Absence of chlorine
	Alternate Method: Make a loop in the end of a copper wire and heat it in a nonluminous flame until the flame is no longer colored. (The wire becomes coated with a film of copper oxide.) Cool the loop and dip it into a little of the powdered sample. Place loop in edge of flame and observe any color change in the flame.	R-3.1	Green color imparted to flame	Presence of chlorine
		R-3.2	Green color not imparted to flame	Absence of chlorine
Nitrogen test	**Place a small quantity of weathered** ...			

			a little water is added	
Beilstein test for chlorine (T-3)	Heat a small porcelain boat (held by pliers) in a nonluminous flame until flame is no longer colored. Cool the boat, add a small sample of weathered paint, and cover it with copper oxide wire fragments. Place boat in edge of flame and observe any color change in the flame.	R-3.1 R-3.2	Green color imparted to flame Green color not imparted to flame	Presence of chlorine Absence of chlorine
	Alternate Method: Make a loop in the end of a copper wire and heat it in a nonluminous flame until the flame is no longer colored. (The wire becomes coated with a film of copper oxide.) Cool the loop and dip it into a little of the powdered sample. Place loop in edge of flame and observe any color change in the flame.	R-3.1 R-3.2	Green color imparted to flame Green color not imparted to flame	Presence of chlorine Absence of chlorine
Nitrogen test (T-4)	Place a small quantity of weathered paint in a small test tube and cover it with twice the quantity of anhydrous calcium oxide or sodium calcium hydrate. Heat the test tube in a flame until fumes are emitted. Place a piece of moist red litmus paper in the mouth of the tube and note any change in color.	R-4.1 R-4.2	Litmus paper turns blue Litmus paper does not change color	Presence of nitrogen Absence of nitrogen
Lead test (T-5)	Place a drop of 8% aqueous sodium sulfide solution[a] on the test surface or on a few fragments of paint and observe any color change. The surface of smooth or hard paint that is impervious to water should be abraded by sanding or scratching.	R-5.1 R-5.2	Specimen turns black or dark gray No darkening of the specimen	Presence of lead Absence of lead
Mercury tests (T-6)	Place a small sample of weathered paint in a small test tube, beaker, or in the well of a glass or ceramic spot plate. Carefully add 2 drops of concentrated nitric acid. Five minutes later, add 4 drops of water and stir with a small glass rod. Withdraw a drop of the clear supernatent liquid and place it on the center of a piece of cuprous iodide paper.[b] Note any color change to paper.	R-6.1 R-6.2	Paper turns orange Paper does not change color	Presence of mercury Absence of mercury
	Alternate Method: Place a small sample of weathered paint in a small aluminum weighing dish. Extract the sample by covering it with a few drops of acetone. When most of the acetone has evaporated add another few drops and also allow them to evaporate.[c] Cover the extracted chips with enough 4% sodium hydroxide solution[a] to cover the entire area previously covered by the acetone. Allow the reaction (tiny bubbles of hydrogen evolving) to continue for 3 minutes. Gently rinse away most of the sodium hydroxide solution by filling the aluminum dishes once with distilled water and carefully pouring it off immediately afterwards. Care must be taken not to dislodge the thin film of mercury which is deposited onto the aluminum. Permit the dishes to dry in an area free of air currents. Approximately an hour later, visually check the treated area for deposits of aluminum oxide that puff up and pockmark the surface. The deposits are white when pure, but may have a grayish tinge like cigarette ashes; the texture resembles cigarette ash.	R-6.1 R-6.2	White to gray deposits of aluminum oxide No deposits of aluminum oxide	Presence of mercury Absence of mercury

[a] By weight of chemical in water.

[b] Cuprous iodide paper is prepared by adding a few drops of an aqueous suspension of cuprous iodide to a piece of thick filter paper one square inch or more in area. Directions for preparing the suspension of cuprous iodide are given in Reference 7. The procedures are rather complicated for the field, but the suspension can be stored for 6 months if it is protected from light. The cuprous iodide test paper itself can also be stored for at least 2 months under the same conditions.

[c] The evaporation can be accelerated by heat or with a stream of air.

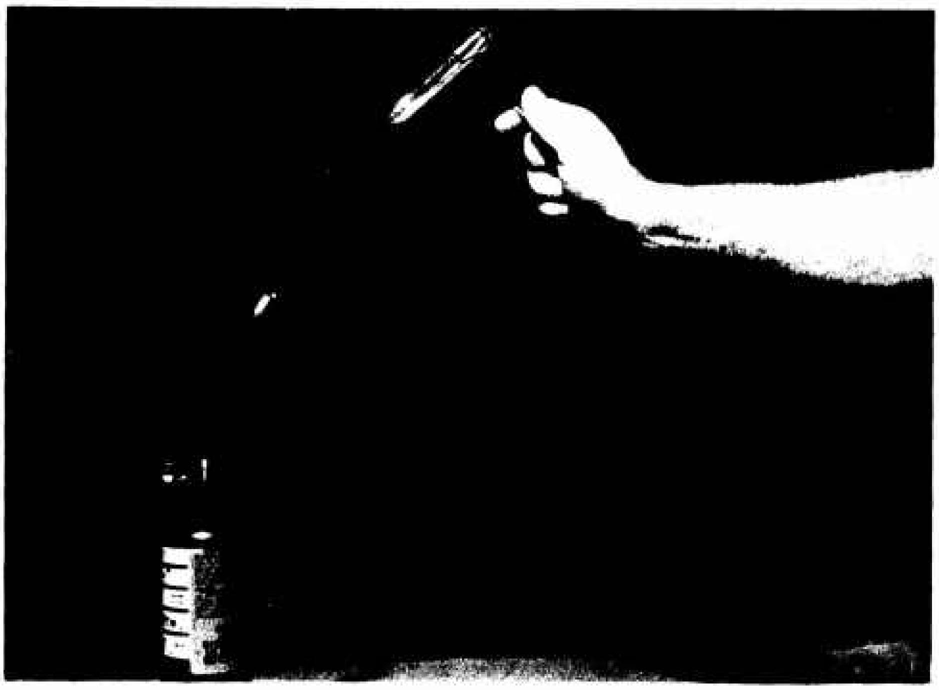

Figure 2. Pyrolyzing sample of weathered paint.

Figure 3. Formation of phthalic anhydride crystals.

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Casein and polysulfide paints both evolve hydrogen sulfide during pyrolysis, and this gas can be readily identified by an odor like that of rotten eggs or by the rapid darkening of moist lead acetate paper held in the pyrolysis fumes. Although casein and polysulfide paints are not likely to be specified for use at shore activities, inexpensive casein paints might be used as a substitute for or component of interior latex paints. Also, the test itself is very simple. The test result is, therefore, described even though it was not employed to test the 61 samples of cured or weathered paint films.

Solubility Test (T-2)

Paints of the Class II category cure by simple evaporation of an organic solvent, undergoing no chemical change. Thus, unless the resins of Class II paints are drastically changed by weathering, they can be redissolved in a solvent. Paint pigments are ordinarily inorganic and, thus, are insoluble in organic solvents. Rapid disintegration of black paint fragments and dispersion of the pigment suggest that the binder is asphalt or coal tar. Solubility tests were run using benzene, chloroform, cyclohexane, methylethyl ketone, butyl acetate, and turpentine as solvents. Benzene and methylethyl ketone proved to be the best choices for identification purposes.

Beilstein Test for Chlorine (T-3)

When an organic chlorine compound and copper oxide are heated together in a nonluminous flame, copper chloride is formed and volatilized to impart a green color to the flame. Other halogen compounds and cyanide compounds also impart this color, but they are not very likely to be present in weathered paint. The intensity and duration of the green coloration are indicative of the relative amount of chlorine in the sample.

Nitrogen Test (T-4)

When organic compounds containing nitrogen are mixed with anhydrous calcium oxide (quick lime) or sodium calcium hydrate and are strongly heated with limited access to air, they usually emit ammonia fumes. The ammonia can be detected by placing a piece of moist red litmus paper in the fumes and observing whether it turns blue.

Lead Test (T-5)

Lead pigments have been used extensively in paints to impart hiding power and to prevent corrosion of underlying iron or steel. Lead driers are used in smaller quantities to accelerate drying of oxygen-curing paints. A disadvantage is that lead pigments, and lead driers to a much lesser extent, darken in areas where the air contains traces of hydrogen sulfide. Another disadvantage is that lead compounds are toxic and can be accidentally injested by children chewing on painted surfaces. A simple test (Figure 4) for detecting lead in paints was developed at the University of Rochester,[9] and is described in Table 2.

Mercury Tests (T-6)

Mercury biocides are frequently incorporated into latex paints to prevent biodegradation during storage. They are also frequently incorporated into paints to provide mildew resistance. Because of possible adverse environmental effects, nonmercurial biocides are currently being investigated. For this reason a test for the presence of mercury is important.

The development of an orange color by the reaction of mercury compounds with cuprous iodide is a good identification test (Figure 5). In the procedure described in Table 2, the color deepens with time and has a maximum intensity after about one-half hour.

An observation at NCEL led to the development of a new test for mercury in paints. This test, based upon the fact that mercury salts catalyze the corrosion of aluminum (Figure 6), is a little less sensitive than the cuprous iodide test, but it is easier to perform. Table 2 explains the test procedure.

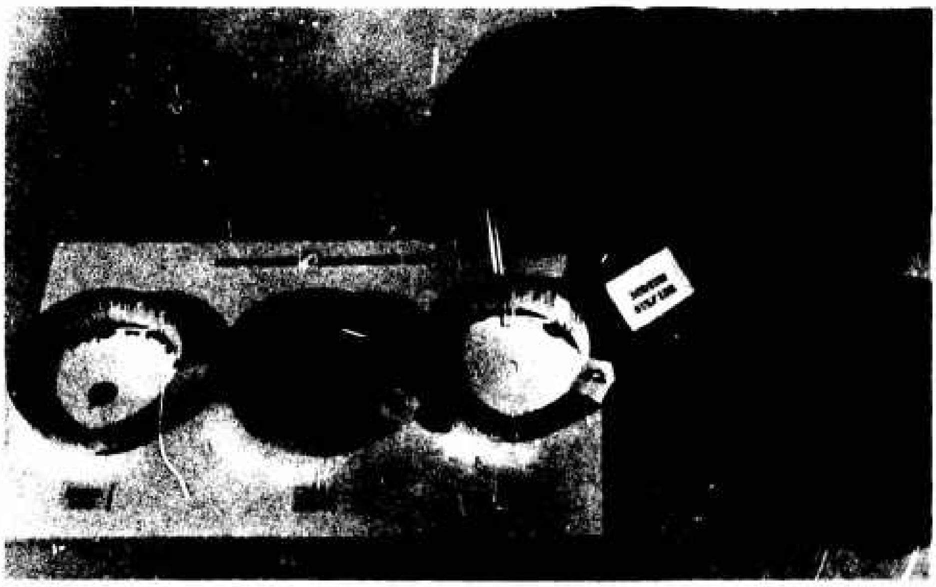

Figure 4. Sodium sulfide test for lead.

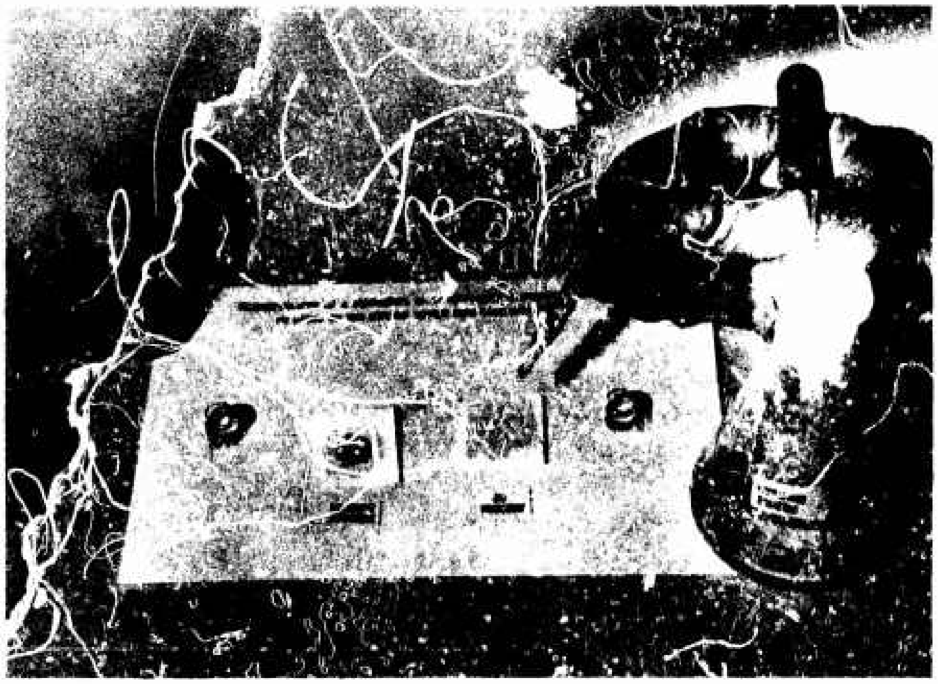

Figure 5. Cuprous iodide test for mercury.

Figure 6. Aluminum test for mercury.

EXPERIMENTAL RESULTS

Table 3 identifies the 61 samples of weathered paint tested and summarizes most of the test results. Upon pyrolysis (Test T-1), 58 of the 61 samples emitted some smoke and tar, indicating that they were organic. Thus, the three inorganic paints of Class V were distinguished from the others by their lack of smoke and tar (Result R-1.1).

The two nitrocellulose paints decomposed rapidly with a minor, harmless explosion (Result R-1.2) almost immediately after initiation of heating, thus distinguishing themselves from the other 59 paints.

Of the 58 samples producing tar upon pyrolysis,* 15 produced only very small quantities of it (Result R-1.5). These included all polyvinyl acetate and acrylic latex specimens of Class III. About one-third of the lacquers of Class II also emitted only a small quantity of tar, while about two-thirds, including virtually all of the polyvinyl chlorides, produced an abundance of tar (Result R-1.4). Virtually all of the Class I and IV specimens produced an abundance of tar upon pyrolysis.

In the pyrolysis test, only 12 of the 61 samples had needle-like crystals condense on the upper portion of the tube (Result R-1.3). This included all nine known alkyd paints, two nitrocellulose paints specified to also contain an alkyd resin of the noncuring type, and one rare polyester made from orthophthalic acid.

The solubility of all 61 specimens was tested in benzene, methylethyl ketone, cyclohexane, butyl acetate, chloroform, and turpentine. It was found that enough information (Test T-2) could be obtained with the first two of these solvents to identify the paints. All of the Class II specimens were either soluble in methylethyl ketone (Result R-2.1) or benzene (Result R-2.2). The vinyls and saran paints were insoluble in benzene, the nitrocellulose and polyvinyl paints were slightly soluble, and the chlorinated rubber, vinyl toluene—butadiene, asphalt, and coal tar paints were soluble. The latter two materials imparted a dark brown color to either the methylethyl ketone or the benzene (Result R-2.4). The polyvinyl butyral paint was a special case in that it was not readily soluble in dry methylethyl ketone, but immediately dissolved when a little water was added (Result R-2.5).

* This includes the two nitrocellulose paints that decomposed rapidly.

Table 3. Results of Identification Tests on Weathered Paint Samples

Class	Generic Type	Specification	Positive Test Results[a]		
			Pyrolysis	Solubility	Elementary
I	drying oil	TT-P-102, Class A	1.4	2.3	5.1
		TT-P-102, Class B	1.4	2.3	5.1
		TT-P-103	1.4	2.3	–[b]
		TT-P-104	1.5	2.3	5.1
		TT-P-25	1.4	2.3	5.1
		TT-P-86, Type I	1.5	2.3	5.1
	drying alkyd	TT-V-81	1.3, 1.4	2.3	–
		TT-P-115, Type I	1.3, 1.4	2.3	–
		TT-S-179	1.3, 1.4	2.3	–
		TT-E-508	1.3, 1.4	2.3	–
		TT-E-509	1.3, 1.4	2.3	–
		TT-E-543	1.3, 1.4	2.3	–
		TT-P-645	1.3, 1.4	2.3	–
		TT-P-659	1.3, 1.4	2.3	–
		MIL-E-15130	1.3, 1.4	2.3	–
	drying phenolic	TT-E-522	1.4	2.3	–
		MIL-P-15145	1.4	2.3	–
IIA	chlorinated rubber	proprietary	1.5	2.1, 2.2	3.1
		proprietary	1.4	2.2	3.1
	coal tar	MIL-C-18480	1.4	2.2, 2.4	4.1
	asphalt	proprietary	1.4	2.2, 2.4	4.1
		proprietary	1.4	2.2, 2.4	–
	vinyltoluene–butadiene	TT-P-110, Type I	1.5	2.1, 2.2	3.1
IIB	polyvinyl chloride	proprietary	1.4	2.1	3.1
		proprietary	1.4	2.1	3.1
		proprietary	1.4	2.1	3.1
		proprietary	1.4	2.1	3.1
		proprietary	1.4	2.1	3.1
	nitrocellulose	TT-L-50, Type I	1.2, 1.3	2.1, 2.2	4.1
		TT-L-50, Type I	1.2, 1.3	2.1, 2.2	–
	polyvinylidene chloride	MIL-L-18389	1.5	2.1	3.1, 4.1
	polyvinyl butyral	MIL-P-15328	1.5	2.5	–
III	polyvinyl acetate	TT-P-55	1.5	2.3	4.1
		TT-P-29	1.5	2.3	4.1
		proprietary	1.5	2.3	3.1
	acrylic latex	TT-P-19	1.5	2.3	4.1
		TT-P-19[c]	1.5	2.3	4.1, 6.1
		TT-P-19[c]	1.5	2.3	4.1, 6.1
		proprietary	1.5	2.3	4.1
		proprietary	1.5	2.3	4.1, 6.1

continued

Table 3. Continued

Class	Generic Type	Specification	Positive Test Results[a]		
			Pyrolysis	Solubility	Elementary
IV	epoxy	proprietary	1.4	2.3	3.1, 4.1
		proprietary	1.4	2.3	3.1, 4.1
		proprietary	1.5	2.3	4.1
		proprietary	1.4	2.3	3.1, 4.1
		proprietary	1.4	2.3	4.1
		proprietary	1.4	2.3	4.1
		proprietary	1.4	2.3	3.1, 4.1
	coal tar epoxy	proprietary	1.4	2.3	3.1, 4.1
		proprietary	1.4	2.3	4.1
		proprietary	1.4	2.3	4.1
		proprietary	1.4	2.3	3.1, 4.1
	urethane	proprietary	1.4	2.3	4.1
		proprietary	1.4	2.3	4.1
		proprietary	1.4	2.3	3.1, 4.1
		proprietary	1.4	2.3	4.1
		proprietary	1.4	2.3	4.1
	polyester	proprietary	1.4	2.3	4.1
		proprietary	1.3, 1.4	2.3	–
V	zinc silicate	proprietary	1.1	2.3	–
	flame-sprayed aluminum	MIL-M-3800	1.1	2.3	–
	flame-sprayed zinc	MIL-M-3800	1.1	2.3	–

[a] Identification of codes for positive results:

1.1	Inorganic	2.1	Soluble in methylethyl ketone	3.1	Contains chlorine
1.2	Nitrocellulose	2.2	Soluble in benzene	4.1	Contains nitrogen
1.3	Phthalic alkyd	2.3	Insoluble in organic solvents	5.1	Contains lead
1.4	Abundance of tar	2.4	Bituminous	6.1	Contains mercury
1.5	Scant tar	2.5	Soluble in wet methylethyl ketone		

[b] Dashes indicate no positive results were obtained.

[c] With added mercury biocide.

In the Beilstein test for chlorine (Test T-3), 17 of the 61 paints imparted a green color to the flame (Result R-3.1). These included the eight specified to contain a chlorinated resin. One of the others (TT-P-110, Type 1) was specified to contain chlorinated paraffin. The other seven imparted only a trace of green to the flame. They were all proprietary materials which were not expected to contain chlorinated resins, but which no doubt contained other chlorinated products such as chlorinated paraffin plasticizer.

In the nitrogen test (T-4), all epoxy, coal tar epoxy, and urethane paints turned red litmus paper blue (Result R-4.1). A few other specimens also did this, but none of them were in Class I; therefore, this distinguishes Class I from Class IV specimens. All but one of the Class III paints (acrylics and polyvinyl acetates) gave a positive test, but a sample of pure acrylic resin (Lucite plastic) did not. It appears that some constituent other than the resin (for example, nitrogenous thickener or emulsifying agent) is responsible for the positive nitrogen tests for Class III paints.

The sulfide test for detection of lead (T-5) proved to be rapid, easy to perform, and very reliable. The presence of lead was shown (Result R-5.1) to be only in the five specification paints required to contain a white or red lead pigment. They were all in Class I.

Both methods (T-6) of detecting mercury in weathered paints were reliable; a positive test result (R-6.1) was obtained only when mercury was known to be present. The cuprous iodide test proved to be more sensitive than the aluminum oxidation test, but neither proved to be as sensitive as desired. Thus, three paints specified to contain mercury gave a negative aluminum oxidation test, and two of them gave a negative cuprous iodide test (Result R-6.2). However, mercury biocides are reported[10] to be rather rapidly lost from exterior paints during weathering. Positive results were obtained in tests made by either method on cured paints prepared from liquid paint to which 0.3% by weight of phenylmercuric oleate or diphenylmercury ammonium proprionate was added.

IDENTIFICATION PROCEDURE

Separation into Classes

Four relatively simple tests can separate an unknown paint into its class, as shown in Figure 7. These tests, T-1 (pyrolysis test), T-2 (solubility test), T-3 (Beilstein test for chlorine), and T-4 (nitrogen test), should be performed first to determine the class of an unknown paint before its generic identification is attempted.

If the test specimen does not burn or emit smoke on pyrolysis (Result R-1.1), then it is in Class V. Further confirmations of Class V paints are (1) they are insoluble in methylethyl ketone and benzene (Result R-2.3) and (2) that, unless contaminated, they will give negative tests for chlorine (Result R-3.2) and nitrogen (Result R-4.2).

If the test specimen is soluble in methylethyl ketone (Result R-2.1) or benzene (Result R-2.2), then it is in Class II.

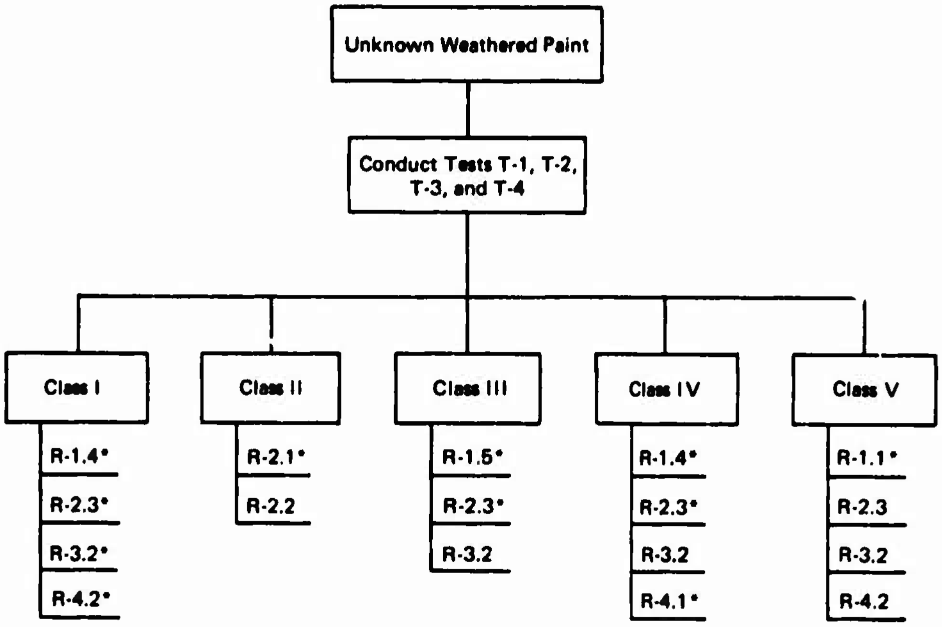

Figure 7. Separation of unknown paints into the basic classes.

If the test specimen gives a relatively small quantity of tar upon pyrolysis (Result R-1.5) and is insoluble in methylethyl ketone and in benzene (Result R-2.3), it is in Class III.

If the test specimen gives an abundance of tar upon pyrolysis (Result R-1.4), is insoluble in methylethyl ketone and benzene (Result R-2.3), and gives a negative test for chlorine (Result R-3.2), it is in Class I or Class IV. Should such a paint give a positive nitrogen test (Result R-4.1), it belongs in Class IV; but it should be noted that not all Class IV paints contain nitrogen. (For example, polyesters in Class IV would not ordinarily give a positive test for nitrogen.) The only other clue in distinguishing Class I from Class IV is that if needle-like crystals form upon pyrolysis (Result R-1.3), the paint is an alkyd and, thus, is in Class I.

Further Identification Within Classes

Class I. All Class I paints contain drying oils, either modified or unmodified. If the paint is modified with phthalic anhydride to form an alkyd, it can be detected by the formation of needle-like crystals upon pyrolysis (Result R-1.3). The identity of other modified or unmodified drying oil paints is difficult to confirm. It should be noted that both alkyd and drying oil–phenolic traffic paints can be modified by adding chlorinated rubber to accelerate drying; they would then give a positive Beilstein test for chlorine (Result R-3.1). Drying oil paints are found most commonly on wood and less commonly on masonry and steel.

Class II. Class II paints can be further subdivided into Classes IIA and IIB according to solubility in benzene and then further identified as to generic type by results of tests T-1, T-2, T-3, and T-4, as shown in Figure 8. Chlorinated rubber, vinyl toluene–butadiene, asphalt, and coal tar paints are soluble in benzene (Result R-2.3), thus placing them in Class IIA; vinyl, vinylidene chloride-acrylonitrile (saran), polyvinyl butyral, and nitrocellulose paints are not soluble in benzene, thus placing them in Class IIB. Chlorinated rubber paints can be distinguished from other benzene-soluble paints in Class IIA by a positive Beilstein test for chlorine (Result R-3.1). Asphalt and coal tar paints are distinctive in Class IIA in that they impart a dark brown color to the solvent when dissolved in methylethyl ketone or benzene (Result R-2.4). Also, they are usually soft paints and can be indented with the fingernail. However, they are difficult to separate from each other by a simple test. Vinyl toluene–butadiene paints can be distinguished from other Class IIA paints by their lack of positive tests for chlorinated rubber (Result R-3.1), and by their lack of asphalt and coal tar (Result R-2.4).

The four Class IIB paints (insoluble, or slightly soluble, in benzene) can easily be distinguished from each other. Vinyl paints give a positive Beilstein test for chlorine (Result R-3.1) and a negative nitrogen test (Result R-4.2). Saran paints give a positive Beilstein test for chlorine (Result R-3.1) and a positive nitrogen test (Result R-4.1). Saran can be further identified by alternate thin layers of orange and white paint and by the fact that it does not usually occur in any other color. Saran paints have been largely replaced by others, but they still are occasionally found on fuel tank interiors. Polyvinyl butyral can be distinguished from other Class IIB paints by the fact that it does not readily dissolve in dry methylethyl ketone, but will dissolve after a little water has been added (Result R-2.5). Nitrocellulose paints can be distinguished from other Class IIB paints by the fact that they decompose rapidly upon pyrolysis (Result R-1.2).

Class III. Two latex paints, acrylics and polyvinyl acetates, are commonly used throughout the Naval Shore Establishment. Acrylic paint can usually be distinguished by the distinctive sickening sweet smell produced upon pyrolysis; the smell can be compared to that of a pyrolyzed authentic sample of acrylic, such as Lucite plastic.

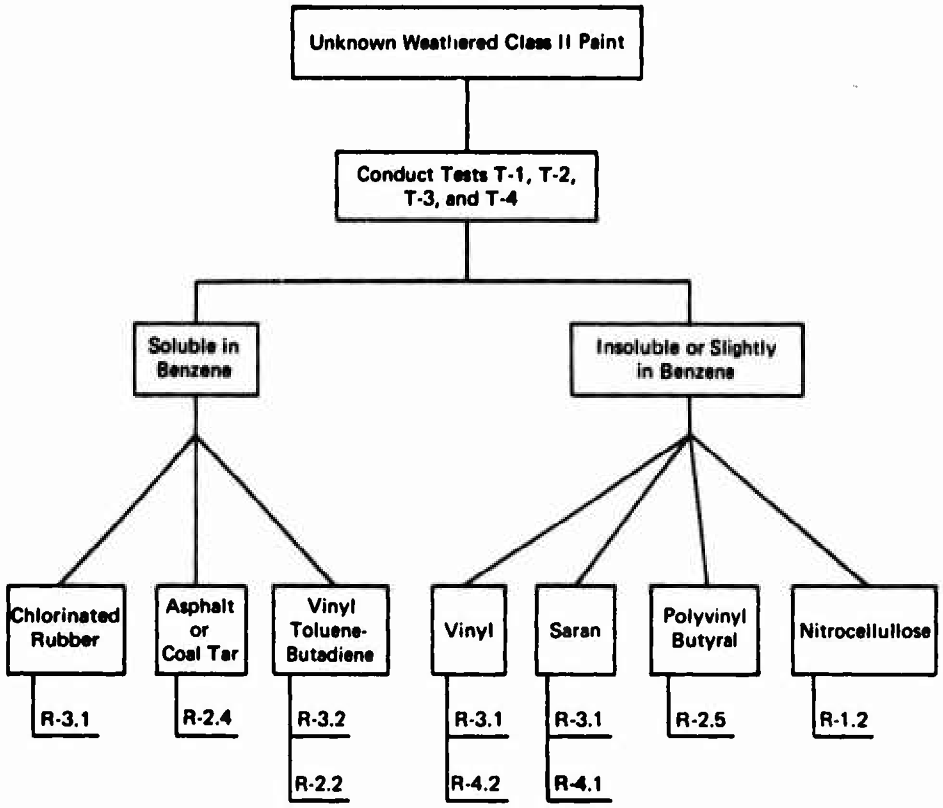

Figure 8. Separation of Class II paints into generic types.

Class IV. Although Class IV paints are generally distinguished from Class I paints by a positive nitrogen test (Result R-4.1), polyesters will not usually give a positive test. However, they are most frequently used with chopped glass fibers, fiber glass cloth, or glass flakes to impart strength or abrasion resistance, and the presence of the glass will aid in their identification. Epoxies are difficult to distinguish from urethanes in a simple test. Coal tar epoxies will be black, except for a few proprietary formulations that have special pigmentation (for example, flake aluminum or brown iron oxide).

Class V. Flame-sprayed metals are relatively rare and are always found on steel. Silicates are most usually found as zinc inorganic silicate paints on steel and have relatively little binder as compared to the amount of zinc dust pigment.

DISCUSSION

The procedure for identifying an unknown weathered paint is not as clean cut as it might appear from the preceding description. Also, paints can be combinations of different generic types, such as alkyd–chlorinated rubber. Thus, field personnel must take advantage of all data available to obtain proper identification. Old work orders or contracts identifying the paints to be used might be available. It is usually much easier to determine if a particular weathered paint is of the specified type than to determine its actual generic type. The substrate and exposure conditions should alert one as to the types of paint likely to have been used. Less expensive paints of the Class I category are more likely to be found in mild environments than the more expensive Class IV paints that are generally used only in aggressive environments. Table 4 lists different types of paint according to their field use. This table is not all inclusive, but includes many of those paints that are commonly used for each application. The manual on paints and protective coatings, NAVFAC MO-110,[2] gives more complete information on paint uses.

While the presence of lead or mercury in a paint will not in itself identify the class of the paint, it can give clues to the identification. Lead is used extensively in Class I paints, and mercury is used extensively in Class III paints. Also, TT-P-102, TT-P-103, TT-P-104, and TT-P-105 are similar in composition, all being drying oil paints, but TT-P-102 and TT-P-104 can be distinguished from the other two in that they contain lead pigments while the others do not.

The test procedures were developed for simplicity and speed. Table 5 lists the equipment and reagents needed for a test kit suitable for use by shore activities. Most of the items are readily available from suppliers of scientific equipment, and their total cost would be about $60.00. Even though the procedure and kit have limitations, they can provide practical information to shore activities. If identification of a paint involves legal aspects, such as corrective action by a contractor, a positive identification by sophisticated analytical procedures is usually necessary. This can be accomplished by a private testing laboratory or by NCEL.

CONCLUSIONS

1. The NCEL procedure for identifying the generic type and general composition of weathered paints is suitable for use by shore activities and can provide much practical information.

2. More specific or legal documentation should be obtained from a laboratory with sophisticated equipment.

Table 4. Listing of Paints According to Use

Area of Use	Paint
Interior metal	Alkyd Chlorinated rubber Epoxy Urethane
Interior plaster and wall board	Acrylic Alkyd Chlorinated rubber
Exterior wood	Drying oil Alkyd
Exterior concrete and masonry	Acrylic Polyvinyl acetate Cement Chlorinated rubber (especially for high humidity and moisture environments) Vinyl (for corrosive environments)
Exterior iron and steel	Oil, Alkyd (relatively mild environments) Drying oil phenolic (for high humidity or rainfall) Vinyl, Zinc inorganic silicate, Epoxy, Urethane (very corrosive or immersed marine environments)
Wooden floors	Drying oil (unmodified or modified with phenolic) Alkyd Urethane
Interior water storage tank	Vinyl Epoxy Coal tar Drying oil–phenolic
Interior concrete tank and reservoir	Vinyl Chlorinated rubber Epoxy
Traffic and airfield marking	Alkyd Alkyd–chlorinated rubber Drying oil–phenolic Vinyl toluene–butadiene

RECOMMENDATIONS

1. The described kit should be used by Navy Public Works Centers and other activities where the information derived could be put into practical use.

2. Shore activities should supply NCEL with comments on the usefulness and limitations of the procedure and test kit so that, along with information on newer paints, the procedure and kit can be updated.

Table 5. Test Kit for Paint Identification

Equipment	Reagents
Beakers, small	Acetone
Boat, porcelain	Acrylic resin (e.g., Lucite)
Brush, small	Benzene
Burner, portable, gas or alcohol	Calcium oxide, anhydrous
Carrying case (optional)	Copper oxide wire fragments
Copper wire	Cuprous iodide aqueous suspension
Knife	Cuprous iodide test paper
Lens, magnifying, hand	Lead acetate test paper
Medicine droppers	Litmus paper, red
Pliers	Methylethyl ketone
Rods, glass	Nitric acid, concentrated
Sample containers	Sodium calcium hydrate
Sandpaper	Sodium hydroxide solution, 4%
Spatula, small (for transferring samples)	Sodium sulfide solution, 8%
Spot plate, glass or ceramic	
Test tubes, small	
Test tube holder	
Weighing dish, aluminum	

REFERENCES

1. Naval Civil Engineering Laboratory. Technical Note N-1143: Use of X-ray diffraction and infrared spectroscopy in paint analysis, by R. W. Drisko and J. B. Crilly. Port Hueneme, Calif., Mar. 1971. (AD 721696)

2. National Paint, Varnish and Lacquer Association, Inc. Guide to United States government paint specifications, 18th ed., compiled by F. Felicione. Washington, D. C., Nov. 1968.

3. Naval Facilities Engineering Command. NAVFAC MO-110: Paints and protective coatings. Washington, D. C., Jan. 1969.

4. National Bureau of Standards. Building Science Series 7: Organic coatings; properties, selection, and use, by A. G. Roberts. Washington, D. C., Feb. 1968.

5. Naval Civil Engineering Laboratory. Technical Report R-490: Protective coatings for steel piling: Results of harbor exposure of ten-foot simulated piling, by R. L. Alumbaugh and C. V. Brouillette. Port Hueneme, Calif., Nov. 1966. (AD 802877L)

6. ————. Technical Note N-989: Glass reinforced polyester coatings for steel in marine atmospheres, by C. V. Brouillette. Port Hueneme, Calif., Sept. 1968. (AD 843139L)

7. F. Feigl. Spot tests in organic analysis, 5th enl. and rev. English ed. New York, Elsevier Publishing Co., 1956.

8. H. A. Gardner and G. G. Sward. Physical and chemical examination of paints, varnishes, lacquers, and colors, 12th ed. Bethesda, Md., Henry A. Gardner Laboratory, Inc., 1962.

9. Newspaper clipping of unknown origin. Anonymous author.

10. P. Whiteley. "Mould resistant decorative paints for the tropics," Oil and Colour Chemists' Association, Journal, vol. 48, 1965, pp. 172-204.